Development of oxidation resistant high temperature NbTiAl alloys and intermetallics

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JOURNAL DE PHYSIQUE IV
Colloque C9, supplément au Journal de Physique III, Volume 3, décembre 1993

Development of oxidation resistant high temperature NbTiAl alloys and intermetallics

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Abstract. — The effect of alloying elements like Ti, Al, Cr, V and Mo on the oxidation resistance of Nb at high temperature (between 700 °C and 1400 °C) has been studied. The value of the parabolic oxide growth constants, $0.1\ g^2/cm^4\ s < K_P < 100\ g^2/cm^4\ s$, depends on the nature and morphology of oxides formed in the external scale. The growth of protective oxides, like alumina, requires a high content of alloying elements, which usually means a lower melting point and the formation of brittle phases.

1. Introduction.

The improvement of aircraft engines efficiency requires the increase of service temperature of various components. The maximum temperature-stress limit combination of nickel base superalloys has almost been reached and an increase of several hundreds degrees of the temperature requires the use of new alloys [1].

New refractory metals are being considered for advanced gas turbine engine applications. Among them, niobium, with its high melting point and moderate density shows a good potential as a base for new aerospace alloys. However, the mechanical properties at high temperature of current commercial Nb alloys are too low and the oxidation resistance has to be improved by adding significant amounts of Ti and Al. Such alloy compositions lead to the formation of ordered intermetallic phases [2].

The strengthening of Nb alloys based on solid solution and on carbide precipitation is detrimental to density and unsufficient. Strengthening by thermodynamically stable and not too brittle intermetallic phases is considered. It requires the study of the nature and structure of the phases in equilibrium and of the transformation temperatures.

The first approach to improve the oxidation resistance of Nb alloys consisted in alloying with elements such as Ti, Cr, V, Mo, Al in order to dope the Nb_2O_5 oxide or to modify its fracture behaviour. This was not sufficient and it appeared that alloying in order to produce a more resistant surface oxide was required [3]. The second approach was to allow the formation of more protective oxides such as $AlNbO_4$ or Al_2O_3. The literature [4] based on the Wagner approach suggests that the critical Al content $(N_{Al})_{crit}$ necessary to form an external alumina scale is related to the oxygen solubility (N_O), and to the oxygen and aluminium diffusivities (D_O, D_{Al}) in Nb-Al. In binary alloys this value is very high and the alloy has to incorporate some elements to reduce N_O and D_O and to increase D_{Al} and thus decrease $(N_{Al})_{crit}$.

The object of this paper is the description of the oxidation behaviour and the effect of some alloying elements like Ti, Al, Cr, Mo and V to improve the oxidation resistance of some Nb ternary alloys at high temperature.

2. Experimental.

The alloys were prepared at ONERA by tungsten-arc melting under an argon atmosphere to form 80 g buttons. They were heat treated or extruded at temperatures up to 1300 °C.

The phase characterisation was made by X-ray diffraction, electron microprobe analysis (EPMA) and by transmission electron microscopy (TEM). Some transition temperatures were determined by differential thermal analysis (DTA).

The mass increase upon oxidation as a function of time was measured by thermogravimetry between 700 °C and 1400 °C in both air and oxygen, with exposure times up to 100 h. Finally, oxidized samples were evaluated by metallography and other techniques mentionned above.

3. Results and discussion.

3.1 THE MICROSTRUCTURE. — A number of ternary alloys, shown in figure 1 [5], has been produced to study the different phases. This paper describes in more details the performance of A, B, C and D alloys (compositions listed in Tab. I). The zirconium content, usual in Nb alloys, lowers the dissolved oxygen contamination forming small internal particles of ZrO_2 oxide.

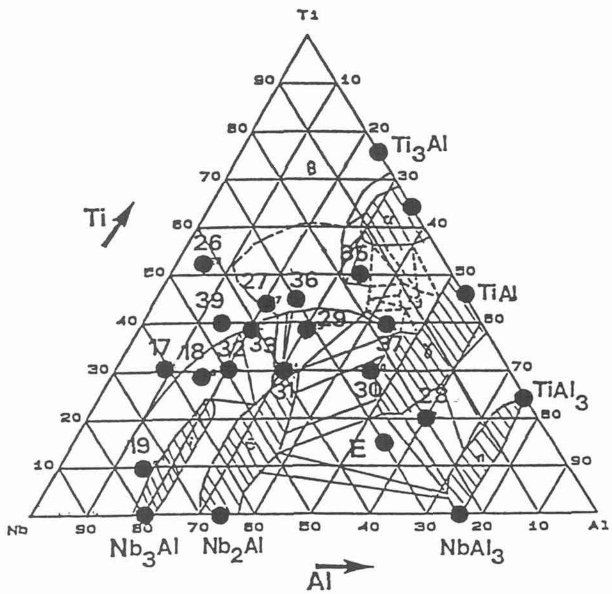


Fig. 1. — NbTiAl ternary phase diagram [5] at 1200 °C with the alloys studied.

Table I. — *Alloys composition (in atomic per cent).*

		Nb	Ti	Al	V	Cr	Zr
	NB 28	19,8	19,8	59,4			1,0
A	NB 29	31,2	38,1	29,70			1,0
B	NB 30	24,7	29,7	44,5			1,0
	NB 31	39,6	29,7	29,7			1,0
	NB 32	49,5	29,7	19,8			1,0
	NB 33	41,1	38,1	19,8			1,0
	NB 34	54,0	30,0	15,0			1,0
C	NB 35	16,5	50,0	32,5			1,0
	NB 36	30,0	46,5	22,5			1,0
	NB 37	16,5	40,0	42,5			1,0
D	NB 38	15,5	36,5	40,0	4,0	3,0	1,0
	NB 39	44,5	40,0	14,5			1,0

Aluminium solubility (between 10% and more than 30% atom.) in bcc Nb is strongly influenced by the Ti content (increases with increasing Ti). For the low Al contents, the δ-Nb_3Al phase is present in the alloys; this phase is stable and hard at high temperature. However, this alloy shows a low oxidation resistance.

When the aluminium content increases, σ-Nb_2Al precipitates in the ordered B2 matrix, alloy A (Fig. 2), or in a $L1_0$ γ-TiAl matrix, alloy B (Fig. 3).

This Nb_2Al phase which can dissolve more than 30% at. of Ti is observed in most of the alloys studied and is detrimental to ductility. The DTA results on A and B alloys, show that σ-Nb_2Al is stable up to 1260 °C in B2 (Alloy A) and up to 1330 °C in γ-TiAl (Alloy B) where an eutectoid reaction occurs: $TiAl + Nb_2Al \rightarrow B2$ (see Figs. 2 and 3). This transition provides a good oxidation behaviour (as shown below) because the aluminium diffusivity is higher in the B2 structure than in the two phase γ-TiAl – σ-Nb_2Al alloy [4].

In order to improve the ductility, other alloys were studied with high titanium content to avoid σ-Nb_2Al or η-$NbAl_3$ brittle phase precipitation. Nevertheless, for the high Ti and Al contents the B2 phase is not stable. For example, alloy C (after heat treatment at 1200 °C), figure 4, contains two different microstructural scales. The coarse scale refers to the microstructure present in the high temperature structure ($B2 + \alpha_2$-Ti_3Al), while on a finer scale we observe a phase transformation of the B2 matrix during cooling, into an omega related phase. This result is in agreement with those of Bendersky *et al.* [6]. Additional studies are necessary to understand the heat treatment sensitive microstructure existing in this part of the ternary diagram.

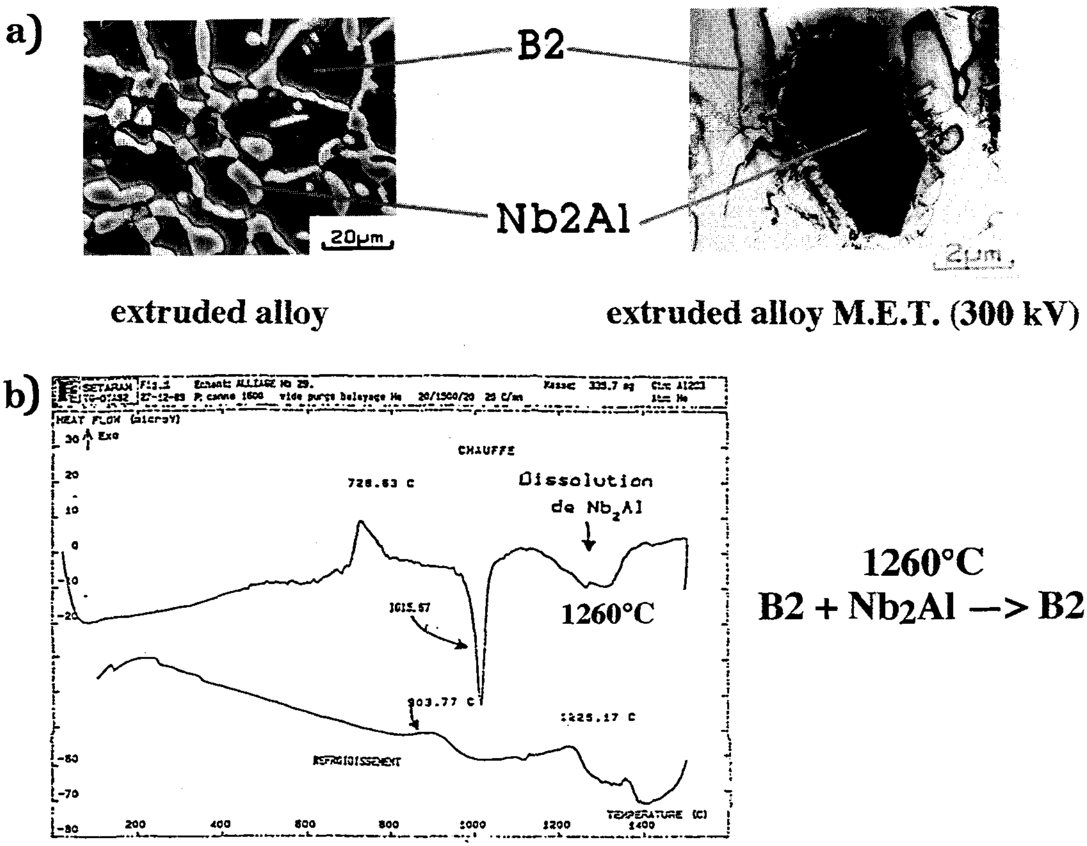


Fig. 2. — a) Microstructure of A alloy. b) Stability of Nb_2Al in B2 matrix (DTA, 20 °C/min).

3.2 OXIDATION BEHAVIOUR. — Study of the oxidation behaviour has permitted to demonstrate the effect of alloying elements like Ti, Al, Cr, V and Mo to improve oxidation resistance at high temperature. On the one hand, we have studied different alloys which had a constant Ti content or a constant Al content or Nb/Ti ratios equal to 0.8. On the other hand, we have studied some intermetallics (Fig. 5).

Figure 5 shows the effect of aluminium additions on the oxidation resistance of alloys. The value of K_p (parabolic oxide growth constant) measured on a time basis up to 100 h, depends on the nature of the oxides formed in the external scale. With 10% of Al, the main oxide is $TiNb_2O_7$. With 20% of Al, a small quantity of $AlNbO_4$ appears. With 30% of Al, $AlNbO_4$ becomes the main oxide. With 44% of Al (Alloy B) the scale morphology (Fig. 6) shows the competition between Al_2O_3, TiO_2 and $AlNbO_4$. At 1200 °C, the diffusivity of Al is not sufficient to allow the formation of a continuous scale of alumina. We can see the precipitation of a subscale of Nb_2Al, resulting from the depletion of Al near the metal-oxide interface, due to a low Al diffusivity. In the case of oxidation at 1400 °C in air, no depletion is observed, and the diffusivity is sufficient to allow the formation of a protective alumina scale.

The addition of a low titanium content (Fig. 7) permits the formation of more protective oxides in the outer scale such as $TiNb_2O_7$ or TiO_2. High contents of Ti increase the aluminium solubility in Nb. Furthermore, with high Al content it stabilizes the B2 phase where

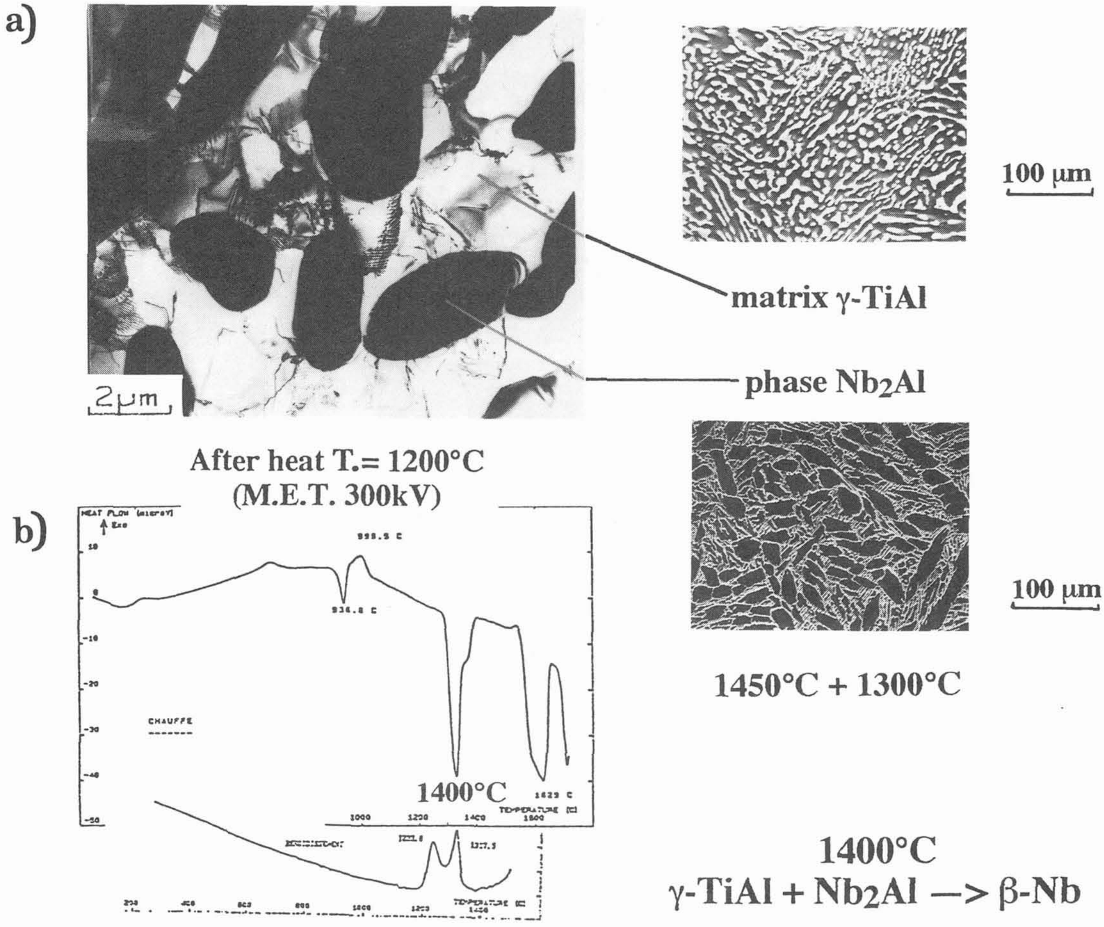


Fig. 3. — a) Microstructure of B alloy. b) Stability of Nb_2Al in γ-TiAl matrix (DTA, 20 °C/min).

Al diffusivity is high. With high aluminium contents at 1000 °C, the increase of Ti improves the oxidation resistance but at 1400 °C an increase of 10% prevents the formation of alumina on NbTiAl alloy containing about 43% of Al and favours the growth of other oxides.

The effect of Cr and V depends strongly on oxidation temperature (Fig. 8). At lower temperatures (1000 °C), the addition of low Cr and V content increases the oxidation rate. At 1200 °C, there is no clear effect, but at high temperatures, such addition produces a decrease of K_p of two orders of magnitude. As discussed above, these elements decrease oxygen diffusivity and solubility in the alloy and enhance the formation of the alumina scale.

Therefore, the addition of low Cr and V contents and high Ti content leads to continuous alumina scale formation for alloy D, (Fig. 9) which does not contain the two brittle phases (Nb_2Al or $NbAl_3$) in opposition with alloy B and with the majority of the alloys studied in the literature.

Other elements are being considered for alloying such as Mo but evaporation of MoO_3 oxides was observed above 800 °C.

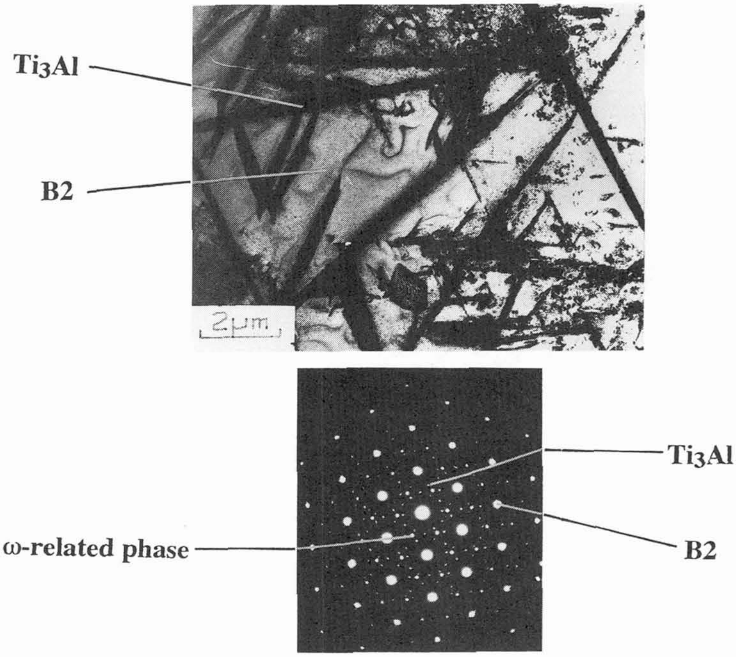


Fig. 4. — Microstructure of C alloy.

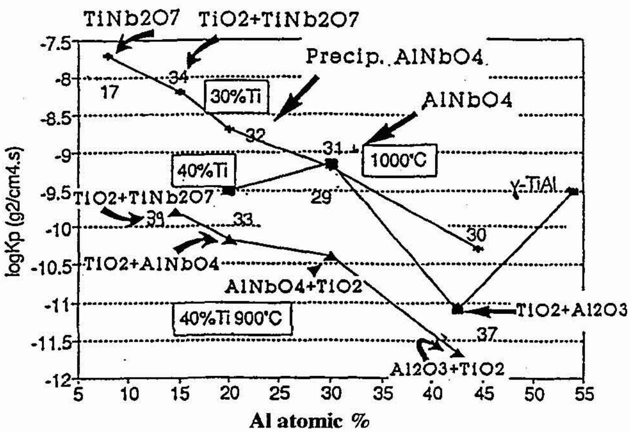


Fig. 5. — Influence of the %Al on the parabolic rate constant. Nb-30, 40%Ti at 900 and 1000 °C in air.

To summarize, we may distinguish 3 domains in the field of experimental variables investigated here (temperature and Al content): i) the first one, where the Al content is smaller than $(N_{Al})_{crit}$ (critical Al content), the main oxide being Nb_2O_5; ii) the second where the Al content is high enough to form an alumina scale but where Al diffusivity in the metal is smaller than in the oxide leading to the formation of other oxides; iii) the third where Al content is greater than $(N_{Al})_{crit}$ and the diffusivity in the metal is greater than in the oxide allowing the formation of a continuous alumina scale. Figures 10 summarizes the different oxides found

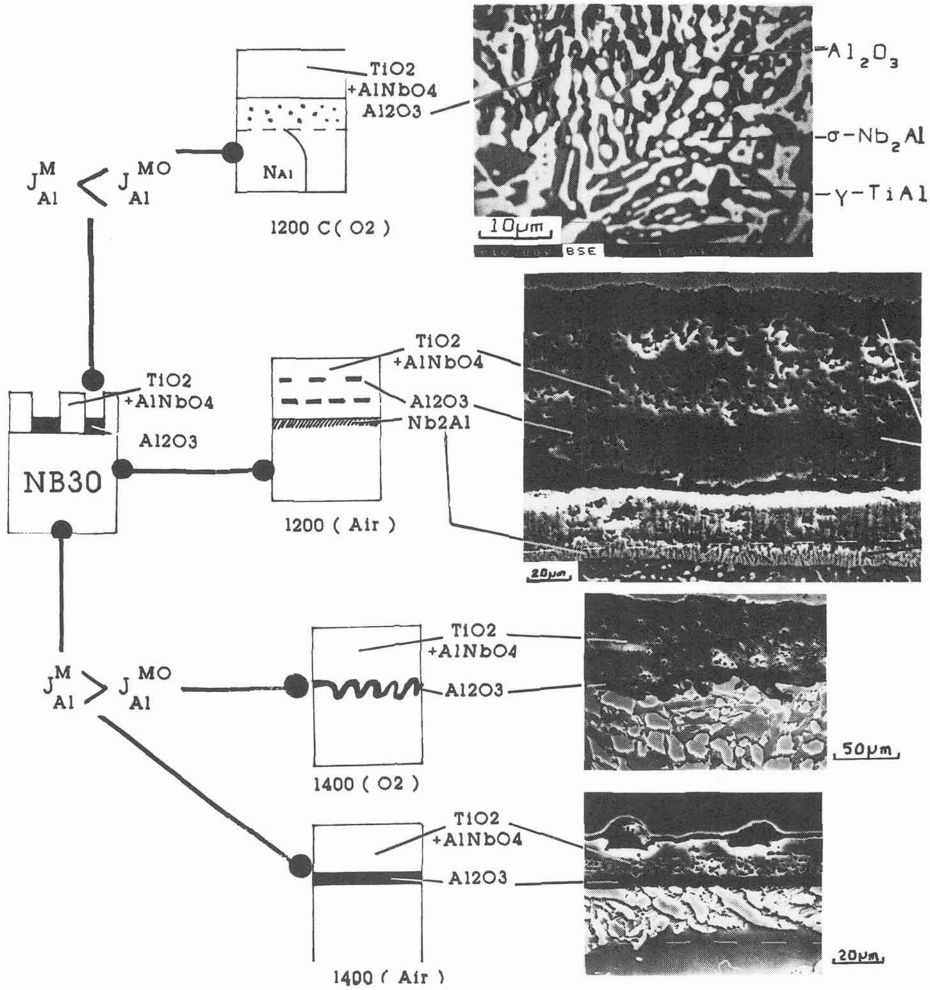
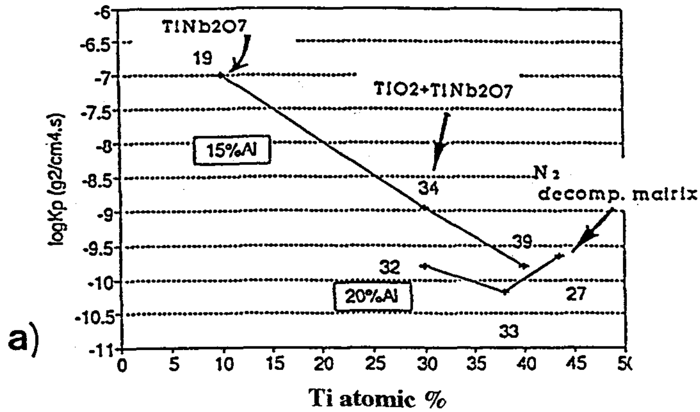


Fig. 6. — Formation of a protective alumina scale on alloy B.

in our ternary alloys. Al_2O_3 is only present in B and D alloys with Al contents of 45 and 40% respectively.

Finally, the effects of oxygen partial pressures and nitrogen environment have been studied. For alloys with high Ti content, binary TiAl intermetallics and Ti rich NbTiAl alloys with low contents in other alloying elements, the oxidation rate is higher in air than in oxygen, showing a nitrogen effect.

On the one hand, for alloys with high Al content, the increase in P_{O_2} produces an increase in oxidation rates at low temperature. At such temperature, internal oxidation, specially of Al, is important. On the other hand, at high temperature, the effect is weak and in the case of alloy D, the temperature required for the transition from internal to external oxidation was lower.



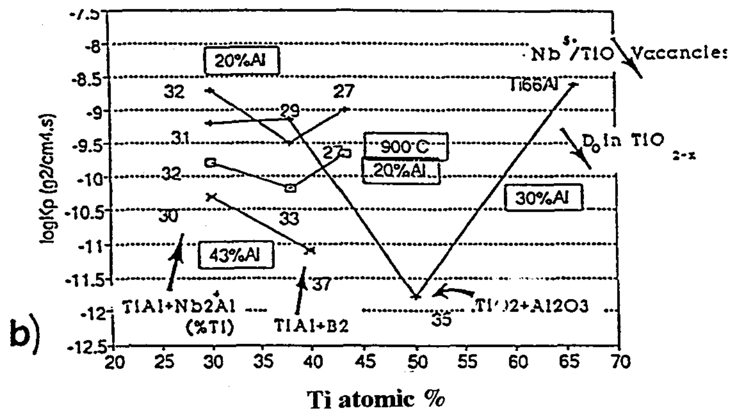


Fig. 7. — Influence of the %Ti on the parabolic rate constant: a) Nb-15, 20%Al at 900 °C in air; b) Nb-20, 30, 43%Al at 1000 °C in air.

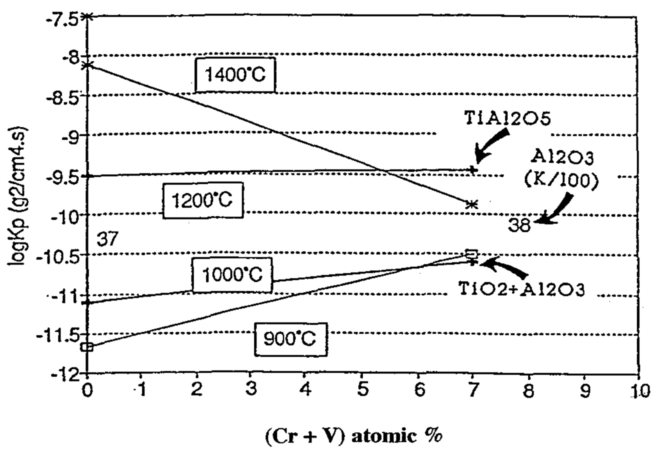


Fig. 8. — Influence of the % (Cr-V) on the parabolic rate constant Nb-40%Ti-42%Al at 1000 °C in air.

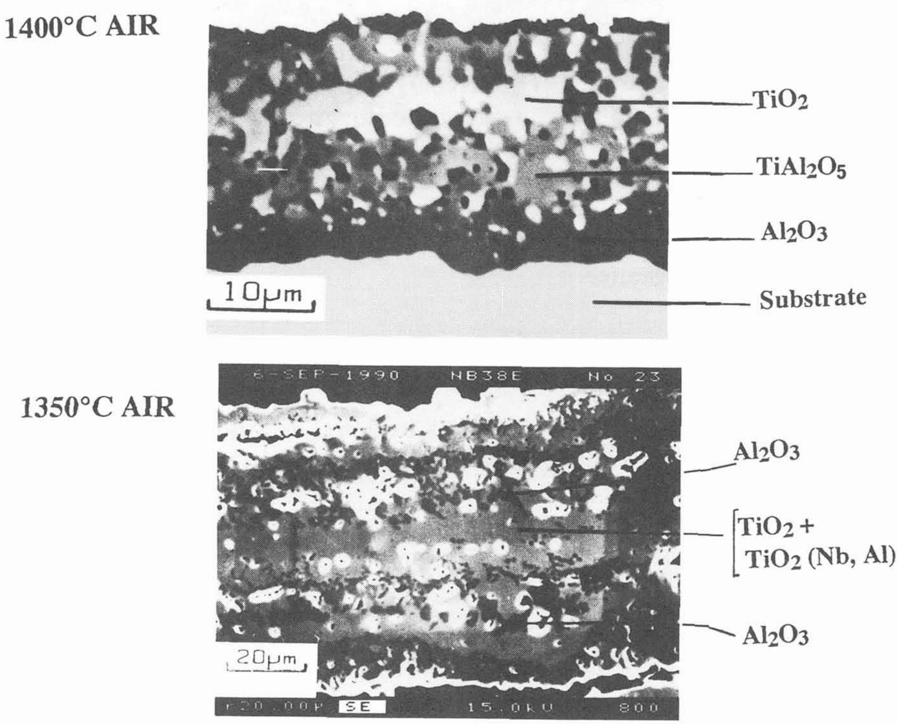


Fig. 9. — Morphology of the oxide scale on alloy D.

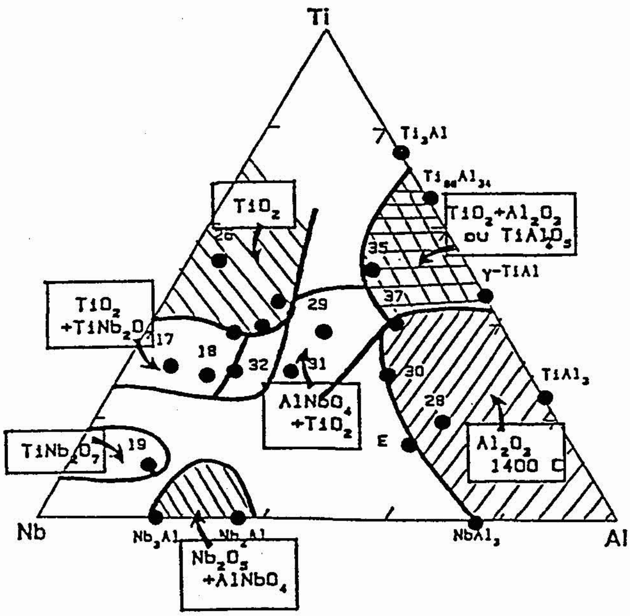


Fig. 10. — Oxide map of NbTiAl alloys at high temperature.

4. Conclusion.

The parabolic rate constants, K_p, depend on the nature and morphology of oxides formed in the external scale, principally $TiNb_2O_7$, $AlNbO_4$, TiO_2 and Al_2O_3 (ranked in the order of increasing oxidation resistance). They are governed by the alloy composition and by diffusivities.

The formation of protective oxides requires a high content of alloying elements (Al, Ti), which may lower the melting point and lead to the formation of brittle phases. We are going to consider next the effect of powder metallurgy manufacturing on microstructure, mechanical properties and oxidation resistance.

Acknowledgements.

This work was supported by the "Direction des Recherches Etudes et Techniques" and by SNECMA. We acknowledge the contribution of ONERA in the manufacturing of test samples and in the design of new alloys.

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